Molecular treatment of charge transfer cross sections in N^{5+} collisions with H_2.

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We present cross sections for electron capture in N^{5+}+ H_2 collisions in the energy range 100 eV/amu$\leq E \leq$ 6keV/amu. We employ a model potential aproximation to treat the interaction of the active electron with the cores, and a recently proposed method, which applies the independent particle model to evaluate the hamiltonian matrix elements.

I. INTRODUCTION

The calculation of charge transfer cross sections in collisions of multiply charged ions with H_2 molecules becomes cumbersome when a large number of coupled states has to be included in the basis. An alternative approach, widely applied in ion-atom collisions (see e.g. [1] and references therein), is the use of effective potentials, as previously applied to ion-H_2 collisions in refs. [2]-[10]. In this work, we consider the collision N^{5+} with H_2. At impact energies E = 100-6000eV/amu, we can assume that the $N^{5+}(1s^2)$ core does not appreciably change during the collision. Accordingly, the interaction of the outer electrons with this core can be represented by means of an effective potential. Besides, and excluding H_2 fragmentation, the interaction of the active electron with the H_2^+ core is represented by a (bicentric) second effective potential, as in refs.[2]-[10]. The simplified method thus obtained involves the solution of a one-electron dynamical problem for the active electron in the field of two effective potentials. Then, a two-electron interpretation is required to evaluate transition probabilities and cross sections for the physical problem starting from the single-electron counterparts. The interpretation most commonly used assumes equivalent electrons [11–13] and expresses the wavefunction as an antisymetrized product of two identical orbitals; as usual, this model will be called in this paper the independent particle model (IPM). However, it is well known that the IPM can yield inaccurate transition probabilities for two-electron processes (such as double electron capture or transfer ionization), and its application to single electron capture transitions at low energies has not been sufficiently analyzed. In this respect, a study on this subject has been recently presented in [14], where a modification of the IPM approach (IPM-SEC) to treat single electron processes has been proposed.

In this work we present single electron capture (SEC) cross sections in N^{5+} collisions with H_2, calculated with the IPM and IPM-SEC approaches. In the dynamical calculation we employ the standard semiclassical impact parameter treatment [1], the isotropic approximation with a collinear nuclear geometry, and our treatment of the vibrational degrees of freedom is carried out in the frame of the Franck-Condon (FC) approximation, whose accuracy for total and partial single electron capture (SEC) cross sections at impact energies E $\geq$ 100 eV amu^{-1}, (nuclear velocities v $\geq$ 0.063 a.u.), was shown in ref. [15].

In the following section we recall the IPM and IPM-SEC formalisms of ref. [14]. Section 3 reports our static (molecular energies) and dynamical (cross sections) data. In the appendix we show the application of the method of ref. [16] to eliminate conical intersections [17]-[24] between the molecular energies.

Atomic units are employed unless otherwise stated.

II. THEORY

The basic assumption of our treatment have been outlined in the previous section. The first step in the application of the IPM to X^{q+}-H_2 collisions is the solution of a one-electron collision problem in which the motion of the active electron is described by the wavefunction $\psi^m(\boldsymbol{r},t)$, which is a solution of the impact parameter equation [1]

$$\left(h^m - \mathrm{i}\left.\frac{\partial}{\partial t}\right|_{\boldsymbol{r}}\right)\psi^m(\boldsymbol{r},t) = 0 \qquad (1)$$

As usual, the ion follows a rectilinear trajectory $\boldsymbol{R} = \boldsymbol{b} + \boldsymbol{v}t$, with impact parameter $\boldsymbol{b}$ and velocity $\boldsymbol{v}$, with respect the midpoint of the H-H internuclear axis. The Hamiltonian h^m includes two model potentials, which describe the interaction of the active electron with the projectile N^{5+} and target H_2^+ core, respectively. To solve equation (1), we expand the wavefunction $\psi^m(\boldsymbol{r},t)$ in terms of molecular orbitals (MO) χ_j, which are (approximate) eigenfunctions of h^m with energies ϵ_j. This close-

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coupling expansion has the form:

$$\psi^m(\boldsymbol{r},t) = D(\boldsymbol{r},t)\sum_j a_j(t)\chi_j \exp(-\mathrm{i}\int_0^t \epsilon_j \mathrm{d}t') \qquad (2)$$

where D($\boldsymbol{r}$,t) is a common translation factor (CTF) [25] [26], which is needed to enforce the boundary conditions.

Integration of the ensuing system of differential equations yields single-electron elastic (p_1), capture (p_c) and excitation (p_{ex}) probabilities.

In order to relate these model probabilities to those for SEC (P^{SC}), double electron capture (P^{DC}) and excitation (P^{EX}) corresponding to the actual two-effective-electron problem, we consider the two-electron impact parameter equation:

$$\left[H - \mathrm{i}\frac{\partial}{\partial t}\right]\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,t) = 0 \qquad (3)$$

In the usual equivalent-electron IPM, H is replaced by the separable Hamiltonian H^{IPM}

$$H^{IPM} = h^m(1) + h^m(2) \qquad (4)$$

and the corresponding solution of (3) is given by the antisymetrized product of two identical orbitals.

$$\Psi^{IPM}(\boldsymbol{r}_1,\boldsymbol{r}_2,t) = ||\psi^m(\boldsymbol{r}_1,t)\overline{\psi^m}(\boldsymbol{r}_2,t)|| \qquad (5)$$

The two-electron transition probabilities are obtained by projecting Ψ^{IPM} onto the corresponding asymptotic forms of the electronic states in the limit $t \to \infty$: The probabilities P^{SC}, P^{DC} and P^{EX} are:

$$\begin{aligned} P^{SC} &= 2p_1p_c \\ P^{DC} &= p_c^2 \\ P^{EX} &= 2p_1p_{ex} \end{aligned} \qquad (6)$$

It can be noted that P^{SC}, obtained from eq. (6), is always less than 0.5 which points to a limitation of the IPM. On the other hand, P^{DC} is often overestimated [1], because of the lack of a correct screening by the model potential in double capture states. To improve the IPM in the treatment of SEC, we draw from the conclusions of Elizaga *et al.* [8] who showed that, when a diabatic molecular basis is employed, there is a simple relationship between matrix elements of H and H^{IPM}. To achieve this connection, we construct a set of diabatic MOs, $\{\chi_j^d\}$ [27], by a unitary transformation of the set $\{\chi_j\}$ of equation (2), so that the radial part of the one-electron dynamical coupling (including the CTF corrections) vanishes. We then construct the set of two-electron wavefunctions $\{\phi_{kl}(\boldsymbol{r}_1,\boldsymbol{r}_2,t)\}$:

$$\phi_{kl} = \frac{N_{kl}}{\sqrt{2}}\left[||\chi_k^d\,\overline{\chi_l^d}|| + ||\chi_l^d\,\overline{\chi_k^d}||\right] \qquad (7)$$

where $N_{kl} = 2^{-1/2}$ for $k = l$ and $N_{kl} = 1$ for $k \neq l$. The 'exact' two-electron wavefunction Ψ is expanded as:

$$\Psi = D(\boldsymbol{r}_1,\boldsymbol{r}_2,t)\sum_{kl} c_{kl}(t)\phi_{kl}(\boldsymbol{r}_1,\boldsymbol{r}_2)\exp[-\mathrm{i}\int_0^t E_{kl}\mathrm{d}t'] \qquad (8)$$

with $E_{kl} =< \phi_{kl}|H|\phi_{kl} >$. Substitution of (8) in (3) yields a system of differential equations for the expansion coefficients c_{jk}:

$$\mathrm{i}\frac{\mathrm{d}c_{jk}}{\mathrm{d}t} = \sum_{lm} c_{lm} < \phi_{jk}D(\boldsymbol{r}_1,\boldsymbol{r}_2,t)|H - \mathrm{i}\frac{\partial}{\partial t}|\phi_{lm}D(\boldsymbol{r}_1,\boldsymbol{r}_2,t) > \times \exp[-\mathrm{i}\int_0^t (E_{lm} - E_{jk})]\mathrm{d}t' \qquad (9)$$

Then, as shown in [14], at not too low R, the matrix elements of H in eq. (9) can be replaced by those of H^{IPM} of eq. (4), yielding SEC and excitation transition probabilities. The ensuing approximation was called IPM-SEC in [14] to distinguish it from the usual IPM. In practice, the computational effort is similar for both methods, while the new approach is more accurate: for instance P^{SC} can be larger than 0.5. Furthermore, for systems where the interactions between both the entrance channel and SEC functions with DEC functions are not effective, these DEC functions can be removed from expansion (8).

III. CALCULATIONS.

In a similar way as for C^{4+} + H_2 collisions previously treated in reference [14], the electronic states of interest (the entrance channels and the single capture states dissociating into N^{4+}($1s^2$n=3,4) + H_2^+) lie asymptotically above several ionization thresholds (N^{4+}($1s^2$2l)+ H_2^{2+}). Therefore, as in the previous work of reference [14], to obtain *ab initio* molecular data we have employed a block-diagonalization technique (see ref. [15]) to remove the states of the molecular Rydberg series which disociate into N^{3+} ($1s^2$2lnl) + H_2^{2+} and N^{4+} ($1s^2$2l) + $H_2^+(n\lambda)$. Our results are illustrated in fig. 1, where we have plotted the electronic energies of the first states obtained in the block diagonalization calculation for the collinear geometry and for an H-H internuclear distance of 1.4 a.u. From these data, and given the large number of potential energy surfaces found in a narrow energy interval, it is very difficult to carry out a close-coupling treatment in terms of ab initio molecular wavefunctions. This difficulty has led us to study the application of model potential techniques to this problem, as discussed in the previous section. In our model calculation, the mono-

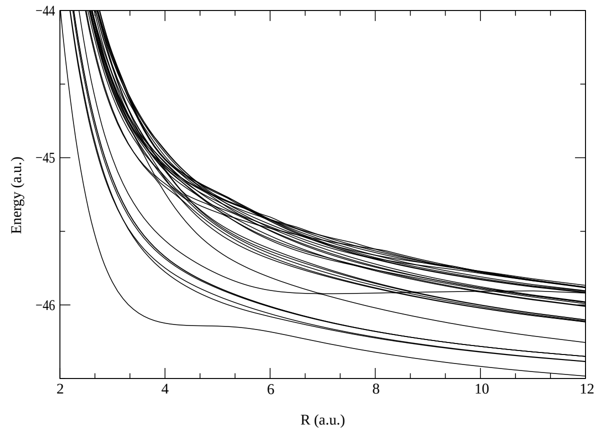

FIG. 1: energies of the electronic states of the NH_2^{5+} quasimolecule for the collinear geometry and for a fixed H-H internuclear distance of 1.4 a.u., as functions of the distance R from the N nucleus to the midpoint of the H-H internuclear axis.

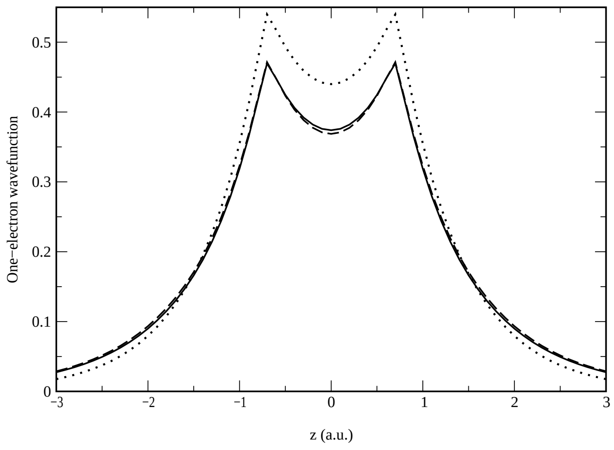

FIG. 2: Plot of the H_2 one-electron wavefunctions as functions of the electronic coordinate z for $x = y = 0$: $(\cdots)$, $1s\sigma_g$ orbital of H_2^+; (- - -) , natural orbital obtained from a full Configuration Interaction calculation; (—) , model potential orbital obtained in the present two-centre model potential calculation.

electronic Hamiltonian h^m (eq.(1)) includes two model potentials V_N and V_H representing the interactions of the active electron with the N^{5+} and H_2^+ cores respectively. We have employed model potentials of the form:

$$V_k = -\frac{Z - N_c}{r_k} - \frac{N_c}{r_k}(1 + \alpha_k r_k)\exp(-\alpha'_k r_k) \qquad (10)$$

For V_N, $r_k = r_N$ is the distance from the electron to the N nucleus, $N_c = 2$, and $Z = 7$, $\alpha_N = 4.3982$, $\alpha'_N = 2\alpha_N$. Unlike previous works [8, 14], where a monocentric model potential was used to represent the interaction with the H_2^+ core, in the present calculation to improve the representation of the H_2 target, two model potentials with N_c=0.5, $Z = 1$ and α=1.6183, were centered on the two H nuclei. The α value was obtained by fitting the H_2 ionization potential for a fixed internuclear distance of 1.4 a_0. The improvement obtained in the description of the entrance channel ($^1\Sigma_g^+$ of H_2) is shown in figure 2: the excellent comparison between the lowest root of the improved model hamiltonian and the natural orbital obtained with an accurate configuration interaction calculation shows that our description of the entrance channel is accurate enough for the present purposes. The basis set included 8 MOs: five dissociating into N^{4+} (n=3) + H_2^+, the two most important molecular orbital dissociating into N^{4+} (n=4) + H_2^+ and the entrance channel. For an H-H distance of 1.4 a_0, these molecular energies are plotted in figure 3.

Cross sections were obtained by integrating the transition probabilities evaluated using the IPM-SEC and the standard IPM formalisms, and are plotted in fig.4. We include in the figure results of experimental data [29, 31] and previous calculations [2, 9] using effective potentials obtained by fitting the experimental H_2 ionization potential, (the difference between H_2^+ and H_2 energies at their respective equilibrium distances), rather than the vertical ionisation energy according to the FC approximation. Besides, the calculations of refs. [2] and [9] do not use any bielectronic interpretation. Good agreement is found between our results and the experimental ones at high energies. For 100< E <1000eV/amu, our calculations do not reproduce the experimental minimum. This disagreement can be due to the need of including double capture chanels in the calculation since double capture is more important in this system than in those studied before; this inclusion is a non-trivial step in the frame

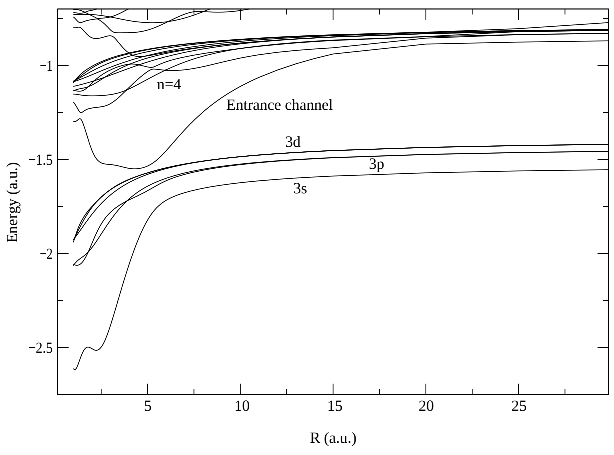

FIG. 3: Correlation diagram for the molecular orbitals obtained in the model potential calculation. The asymptotic limits of the orbitals are shown in the figure.

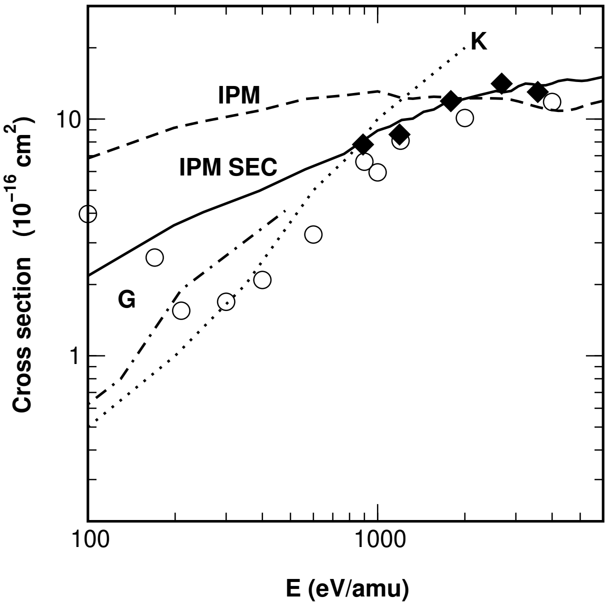

FIG. 4: Cross sections for single electron capture in N^{5+} + $H_2 \to N^{4+}(1s^2 3l)$ + H_2^+ collisions. Present results: lines labelled IPM and IPM-SEC denote results obtained using these methods. G (dashed-dot line) results of [2]; K, ($\cdots$) , results of [9]. ♦, experimental data of reference [29]; ∘, experimental data of reference [31].

the fault can also lie on the experimental side: minima in similar experiments for other systems were explained as due to a limited precision of the measurements (see [30]). Finally, another limitation of our work at low energies is the use of the FC approximation; in this sense, further work is required to check the importance of vibrational effects in the total charge transfer cross section.

IV. APPENDIX: CONICAL INTERSECTIONS (CI) IN N^{5+} + H_2

We now consider the application of the method of ref. [16] to remove conical intersections between molecular energies. We consider in particular transitions between the two states dissociating into $N^{4+}(3p_z)$ + H_2^+ and $N^{4+}(3p_x)$ + H_2^+ in N^{5+} + H_2 collisions.

The adiabatic wavefunctions are accurate approximations to the exact solutions of:

$$H\psi_j(\boldsymbol{r}; R, \boldsymbol{\rho}\,) = E_j \psi_j(\boldsymbol{r}; R, \boldsymbol{\rho}\,) \tag{11}$$

with $\boldsymbol{r}$ denoting the electronic coordinates, R, the distance from the projectile to the midpoint of the H_2 molecule,$\boldsymbol{\rho}$ the H_2 internuclear vector, and H is the Born-Oppenheimer fixed nuclei hamiltonian. (In the present case $H \equiv H^{IPM}$ of eq. (4) and $\Psi_j \equiv \Phi_{kl}$ of eq. (7)) These functions are used as basis to solve the time dependent problem:

$$\left[H - i \left.\frac{\partial}{\partial t}\right|_{\boldsymbol{r},\boldsymbol{\rho}} \right] \Psi(\boldsymbol{r}; R, \boldsymbol{\rho}\,) = 0 \tag{12}$$

along appropriate $\boldsymbol{R}(t)$ trajectories [1] and processes take place through transitions between the adiabatic wavefunctions, induced by rotational ("D_x") and radial ("D_R") couplings.

As shown in [16] these dynamical, or non-adiabatic, couplings are singular at the CI, and it is useful to transform from the adiabatic basis, $\{\psi_1, \psi_2\}$, to a new one $\{\varphi_1, \varphi_2\}$, which does not present the singularities. This is performed through the well known Smith transformation [27].

$$\begin{aligned} \psi_1 &= (\cos\theta)\varphi_1 - (\sin\theta)\varphi_2 \\ \psi_2 &= (\sin\theta)\varphi_1 + (\cos\theta)\varphi_2 \end{aligned} \tag{13}$$

which yields

$$\theta = \frac{1}{2}\tan^{-1}\frac{2H_{12}}{H_{22} - H_{11}} \tag{14}$$

The new (orthonormal) basis functions φ_1, φ_2 are defined so that all their interactions are not singular and present smoothly varying rotational couplings in the linear (or perpendicular) configuration. Their energies $H_{11}(\boldsymbol{R})$ and $H_{22}(\boldsymbol{R})$ cross along a curve that passes through the CI located at R = R_0 and $\alpha = 0$. So, $R - R_0$ and $\alpha\, R$ are the natural independent variables in the ($\boldsymbol{\rho}$, $\boldsymbol{R}$) plane.

In our method we use modified bilinear expressions for all quantities in (4), in the vicinity of the CI, in terms of the independent variables [33]

$$\begin{aligned} H_{22} - H_{11} &= a(R - R_0) + bR|\alpha| \equiv az \\ H_{12} &= c(R - R_0) + dR|\alpha| \equiv d|x| \end{aligned} \tag{15}$$

Near the CI at $x = 0, z = 0$, the adiabatic energies have the double cone form:

$$E_j = \frac{1}{2}\left\{ (H_{11} + H_{22}) + (-1)^j [a^2 z^2 + 4c^2 x^2]^{1/2} \right\} \tag{16}$$

with (j=1,2). Substitution of eq. (15) in eq. (14) yields the expressions for the radial component of the dynamical couplings between the adiabatic wavefunctions, $D_R = \langle\psi_1|\, \partial/\partial R|_\alpha \,|\psi_2\rangle$, in the vicinity of the CI

$$\langle\psi_1| \left.\frac{\partial}{\partial R}\right|_\alpha |\psi_2\rangle - \langle\varphi_1| \left.\frac{\partial}{\partial R}\right|_\alpha |\varphi_2\rangle = \left.\frac{\partial\theta}{\partial R}\right|_\alpha = -\frac{R_0}{R}\frac{ac|x|}{4c^2x^2 + a^2z^2} \tag{17}$$

where the second term, $\langle\varphi_1|\, \partial/\partial R|_\alpha \,|\varphi_2\rangle$, is the remaining, non-singular, part of the coupling. We have a similar expression for the rotational component (D_x) of $\langle\psi_1|\nabla_R|\psi_2\rangle$:

$$\langle\psi_1|\frac{1}{R}\left.\frac{\partial}{\partial\alpha}\right|_R|\psi_2\rangle - \langle\varphi_1|\frac{1}{R}\left.\frac{\partial}{\partial\alpha}\right|_R|\varphi_2\rangle = \frac{1}{R}\left.\frac{\partial\theta}{\partial\alpha}\right|_R = \mathrm{sign}(x)\frac{ac(R-R_0)}{4c^2x^2+a^2z^2} \tag{18}$$

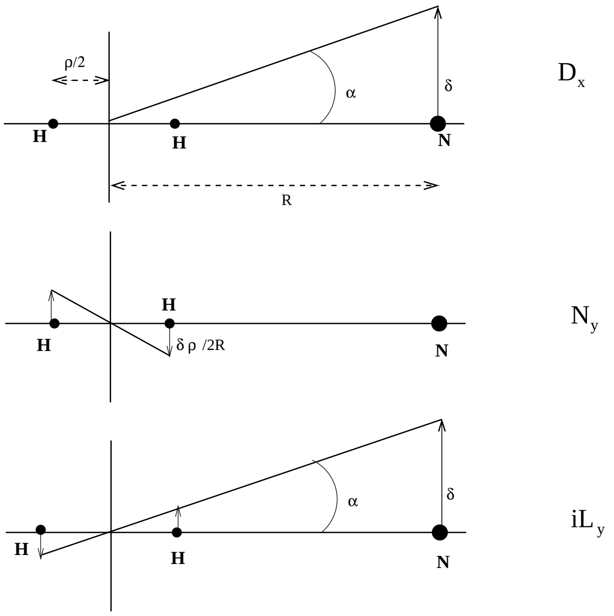

FIG. 5: Plot of the way we calculate the total D_x and the singular (N_y) and regular (iL_y) components of the rotational coupling. The arrows indicate, for each coupling term, the shift of the nuclear positions in the numerical differentiation procedure.

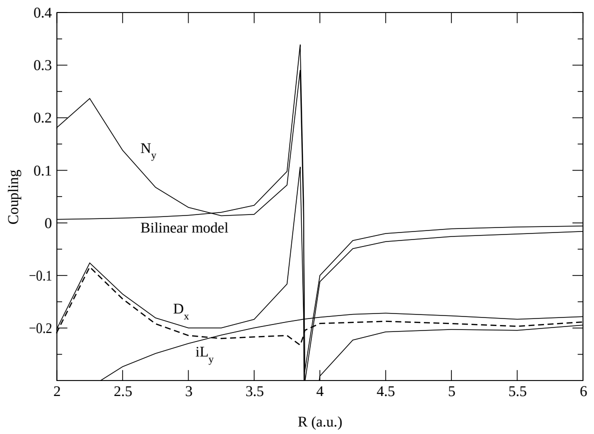

FIG. 6: Total (D_x), and regular iL_y and singular (N_y) components of the rotational coupling between the states $N^{4+}(1s^22p_z) + H_2^+(\sigma_g)$ and $N^{4+}(1s^22p_x) + H_2^+(\sigma_g)$. The dashed line corresponds to the residual coupling between the diabatic states of eq. (18).

The rotational coupling $D_x = \langle\psi_1|\frac{1}{R}\frac{\partial}{\partial\alpha}|_R|\psi_2\rangle$ can be expressed (see ref. [34]), as $D_x = N_y - iL_y$,where the non singular component, iL_y, is the matrix element $<\psi_1|i\mathcal{L}_y|\psi_2>$ of the Y-component of the electronic angular momentum in the molecular-fixed reference frame, and N_y is the singular rotational coupling. We show in fig. 5 an scheme of the way this two components are evaluated numerically.

Next, we have used transformation (14), and equation (16) to check that in the neighbourhood of the CI the bilinear expression (15) is accurate, and to obtain the values for the parameters R_0 = 3.87685, a = 0.04228, b = 5.91498 10^{-5}, c=0.0, and d = 5.3188 10^{-4} in atomic units.

Our method employs the parametrisation of (15) to define the new basis. We then used eqs. (14), (15), and the inverse of eq. (13) to generate the energies and couplings in the modified basis in which φ_1, φ_2 have replaced ψ_1, ψ_2.

The accuracy of expressions (17) and (18) is shown in figs. 6, 7 and 8. In figure 6 we compare the rotational (D_x) couplings calculated in the adiabatic basis, and the parametrised form of equation (18) $\frac{1}{R}\frac{\partial\theta}{\partial\alpha}|_R$ and we show the regular (iL_y) and singular (N_y) components of this coupling. The parametrised (according to eq. (16)) and exact adiabatic energies are compared in figure 7. Figure 8 displays the radial D_R coupling and the corresponding $\frac{\partial\theta}{\partial R}|_\alpha$.

The remaining (regular) rotational component of the residual interaction $\langle\varphi_1|\nabla_R|\varphi_2\rangle$, is also shown in figure 6. As explained before, the new basis also presents couplings through the electronic hamiltonian H, which are given in this method by H_{12} = 5.388 10^{-4} R $|\alpha|$, which is very small except for so large α values that the CI is completely irrelevant.

Acknowledgments

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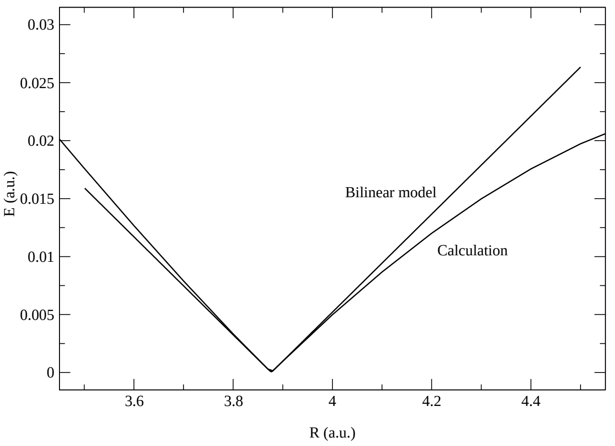

FIG. 7: Calculated and bilinear model (eq. (16)) energy diferences as functions of the projectile-diatomic distance R, for an angle $\alpha = 1\ ^o$, in the vicinity of the CI between the states $\mathrm{N}^{4+}(1s^2 2p_z)$ + $\mathrm{H}_2^+(\sigma_g)$ and $\mathrm{N}^{4+}(1s^2 2p_x)$ + $\mathrm{H}_2^+(\sigma_g)$.

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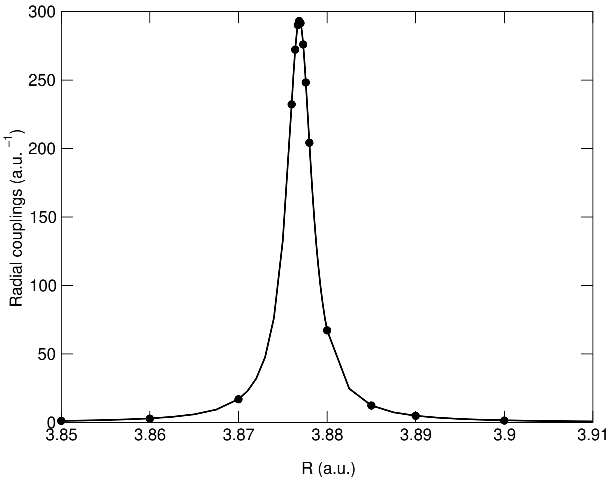

FIG. 8: Comparison between predicted from eq. (17) (line), and calculated (points) radial coupling $\langle\psi_1|\ \partial/\partial R|_\alpha\ |\psi_2\rangle$ between the same states as in fig.7, and $\alpha = 1^o$.

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